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Magnetic headspace adsorptive extraction of chlorobenzenes prior to thermal desorption gas chromatography-mass spectrometry

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Abstract

This study presents a new, user-friendly, cost-effective and portable headspace solid-phase extraction technique based on graphene oxide decorated with iron oxide magnetic nanoparticles as sorbent, located on one end of a small neodymium magnet. Hence, the new headspace solid-phase extraction technique has been called Magnetic Headspace Adsorptive Extraction (Mag-HSAE). In order to assess Mag-HSAE technique applicability to model analytes, some chlorobenzenes were extracted from water samples prior to gas chromatography-mass spectrometry determination. A multivariate approach was employed to optimize the experimental parameters affecting Mag-HSAE. The method was evaluated under optimized extraction conditions (i.e., sample volume, 20 mL; extraction time, 30 min; sorbent amount, 10 mg; stirring speed, 1500 rpm, and ionic strength, non-significant), obtaining a linear response from 0.5 to 100 ng L^{-1} for 1,3-DCB, 1,4-DCB, 1,2-DCB, 1,3,5-TCB, 1,2,4-TCB and 1,2,3-TCB; ~~and~~ from 0.5 to 75 ng L^{-1} for 1,2,4,5-TeCB, ~~1,2,3,4-TeCB~~ and PeCB; and from 1 to 75 ng L^{-1} for 1,2,3,4-TeCB. The repeatability of the proposed method was evaluated at 10 ng L^{-1} and 50 ng L^{-1} spiking levels, and coefficients of variation ranged between 1.5 and 9.5% (n = 5). Limits of detection values were found between 93 and 301 pg L^{-1}. Finally, tap, mineral and effluent water were selected as real water samples to assess method applicability. Relative recoveries varied between 86 and 110% showing negligible matrix effects.

Keywords: Solid-phase microextraction; Chlorobenzenes; Magnetic graphene oxide; Magnetic headspace adsorptive extraction; Gas chromatography-mass spectrometry; Water samples

1 Introduction

Analytical chemists have always benefited from the availability of numerous instruments such as chromatographs, spectrometers, and microscopes, as well as sensors and microdevices. However, these instruments cannot fully satisfy analytical chemists' need to perform trace analysis of analytes of interest in complex matrices. In this respect, one or more pretreatment steps are usually necessary to improve instrument sensitivity and selectivity, referred to as “Sample Preparation”, whose goal is enrichment, clean-up, and signal enhancement [1]. Sample preparation is important in all aspects of chemical, biological, materials, and surface analysis, thus researchers are always looking for more advanced techniques. Notable among recent developments are faster, more economical, more efficient and greener extraction methods like microextraction techniques. In addition, advanced microfabrication techniques have resulted in the development of miniaturized chemical analysis systems, including microscale sample preparation on a chip [2].

Solid-phase microextraction (SPME) is a rapid, solventless and environmentally-friendly extraction technique for the isolation and preconcentration of solutes from liquid, solid or gaseous matrices. Nowadays, many researchers use SPME as an efficient sample preparation technique to extract and subsequently introduce desired analytes into detection instruments such as the gas chromatograph (GC) and liquid chromatograph (LC) with different detectors [3–6]. At first, SPME was used to analyze volatile compounds using fused silica fibers [7], but nowadays, its use has been extended to the analysis of a wide range of analytes from volatile to nonvolatile compounds using uncoated and

coated fibers with liquid and solid phases [4–6,8]. The SPME process comprises two steps: In the first, the fiber is exposed to the sample or its headspace and the target analytes partition from the sample matrix to the coating. In the second step, the fiber bearing the concentrated analytes is transferred to the analytical instrument (e.g., GC or LC) where desorption, separation, and quantification of the extracted analytes take place [9,10].

However, any technique has its drawbacks. Some disadvantages of SPME are: (i) fibers are fragile and can easily be broken; (ii) conditioning should always be performed on each new fiber or when a fiber has not been used for some time; (iii) when a high percentage of suspended matter is present in the sample, the fiber coating can be damaged during agitation, and; (iv) high-molecular-mass compounds can adsorb irreversibly to the fiber, thus changing the properties of the coating and making it unusable, although the latter has been somewhat resolved by over coated fibers. However, the main restriction of SPME is the small amount of sorbent present on the fiber, which leads to certain sensitivity problems [11–13], thus limiting extraction capacity and, consequently, sensitivity cannot be increased by increasing sample volume. To overcome these problems, there are certain modifications to conventional SPME, based on other configurations of SPME and miniaturization of the conventional solid-phase extraction method such as micro-solid-phase extraction (μ-SPE) [14], stir-cake sorptive extraction (SCSE) [15], rotating-disc sorbent extraction (RDSE) [16], stir-rod sorptive extraction (SRSE) [17], stir-bar sorptive extraction (SBSE) [18], microextraction by packed syringe (MEPS) [19], dispersive μ-SPE (dispersive μ-SPE) [20] and headspace sorptive extraction (HSSE) [11,21].

However, all the techniques named above not only present advantages, but also have some drawbacks such as commercial dependence, high cost, complex set-ups, difficult handling, small or limited amount of sorbent, among others. Therefore, the purpose of the present manuscript is to present magnetic graphene oxide (MGO) nanomaterial as sorbent supported on a neodymium magnet (Nd), providing a new extraction technique called Magnetic Headspace Adsorptive Extraction (Mag-HSAE), which overcomes the drawbacks of most of the extraction techniques described above.

One of the advantages of the developed technique is that Nd magnets were used instead of traditional stir bars (which are relatively more expensive and weaker than Nd magnets) to prevent any magnetic nanomaterial leakage, and to fix the extraction material (MGO). In addition, it should be pointed out that MGO was chosen as adsorbent because of its relatively low production cost, easy manipulation, simple synthesis procedure, wide accessibility, and high extraction capacity of aromatic compounds [22–24]. In this work, as model compounds, nine chlorobenzenes were successfully separated and preconcentrated from water samples using Mag-HSAE prior to thermal desorption gas chromatography-mass spectrometry (TD-GC-MS) as a separation/detection system. The results showed that by using relatively cheap Nd magnets, MGO and the proposed set-up rapid and easy handling extraction, stability of the sorbent, high extraction capacity and high sensitive determination of the investigated chlorobenzenes was achievable under the optimized conditions. To our knowledge, this is the first time that Mag-HSAE has been reported.

2 Experimental

2.1 Chemicals and real samples

Nine chlorobenzene compounds were used in the present work, namely: 1,2-dichlorobenzene (1,2-DCB), 1,3-dichlorobenzene (1,3-DCB), 1,4-dichlorobenzene (1,4-DCB), 1,2,3-trichlorobenzene (1,2,3-TCB), 1,2,4-trichlorobenzene (1,2,4-TCB), 1,3,5-trichlorobenzene (1,3,5-TCB), 1,2,3,4-tetrachlorobenzene (1,2,3,4-TeCB), 1,2,4,5-tetrachlorobenzene (1,2,4,5-TeCB), and pentachlorobenzene (PeCB), all obtained from Riedel-de Haën (Seelze, Germany). 1,4-dibromobenzene (1,4-DBB) as internal standard (IS) was also purchased from Riedel-de Haën. All chlorobenzenes and the internal standard were dissolved in HPLC-grade acetonitrile available from Scharlau Chemie (Barcelona, Spain) at 100 mg L^{-1} to obtain stock solutions. These solutions were kept in the dark at 4 °C. Multicomponent working standard solutions were freshly prepared from the stock solutions for each experiment in deionized water (resistivity of 18.2 MΩ cm at 25 °C), supplied using a water purification system (Milli-Q Biocel A10) from Millipore (Billerica, MA, USA).

For the synthesis of the magnetic materials, graphene oxide (GO), $FeCl_3 \cdot 6H_2O$ and $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ from Sigma-Aldrich (St. Louis, MO, USA), and ammonium hydroxide solution (32%, w/w) and ethanol from Merck (Darmstadt, Germany) were used. To adjust ionic strength of the aqueous samples, sodium chloride from Merck was used. For GC-MS measurements, high-purity helium (99.9999%) from Air Liquide (Valencia, Spain) was used as a carrier, for both thermal desorption and GC processes. Liquid nitrogen, also from Air Liquide, was used as a coolant for the cooled GC injection system.

Tap water sample from San Vicente del Raspeig (Alicante, Spain), a mineral water sample from a local supermarket (Alicante, Spain) and an effluent water sample from a municipal wastewater treatment plant (Alicante, Spain) were used as real water samples. The water samples were collected in 1 L Pyrex borosilicate amber glass containers, and stored in the dark at 4 °C until their analysis. In the case of the effluent water, the sample was filtered through syringe filters (Acrodisc®, pore size 0.45 μm) before extraction.

2.2 Apparatus and instruments

Size and morphological properties of the synthesized magnetic nanomaterial were investigated using a transmission electron microscope (TEM) from JEOL Co. (JEM-2010, 200 KV, Tokyo, Japan). The crystal structure of the synthesized nanomaterial was determined by an X-ray diffractometer (XRD, D8-Advance, Bruker Daltonics Inc., Billerica, MA, USA) at room temperature. SQUID magnetometer MPMS-XL-5 (Quantum Design, San Francisco, CA, USA) was used for magnetic characterization. A 35 kHz universal ultrasonic cleaner water bath (Elma, Singen, Germany) was used for the nanomaterial synthesis.

For GC-MS measurements, a Gerstel TDS 2 thermodesorption system equipped with a Gerstel CIS-4 cooled injection system programmable temperature vaporization inlet from Gerstel (Mülheim an der Ruhr, Germany) was

used to carry out the thermal desorption process. It was installed in an Agilent 6890 N gas chromatograph coupled to an Agilent 5973 mass spectrometry detector, both from Agilent Technologies (Palo Alto, CA, USA), which were employed for the analytical measurements. A Gerstel thermal desorption (TD) glass tube (187 mm length, 4 mm I.D., 6 mm O.D.) and glass wool from Panreac (Barcelona, Spain) were used to construct the thermal desorption device (Fig. 1), which enabled the desorption of the compounds from the magnetic nanomaterial, while preventing them from entering the GC system.

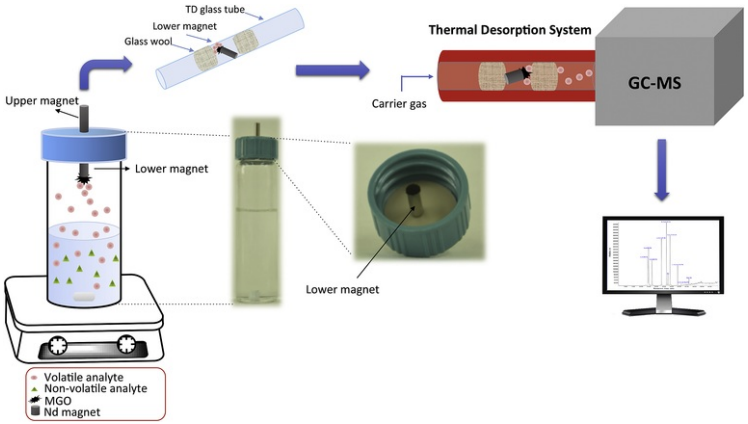

Fig. 1 Scheme of the proposed method.

alt-text: Fig. 1

For the headspace extraction unit, rod shape NdFeB magnets (Nd) (N48, Ø 3 mm, height 8 mm with a nickel-plated (Ni-Cu-Ni) coating) from Supermagnete Co. (Gottmadingen, Germany), and 25 mL glass vials (screw top with solid green Melamine cap with PTFE liner) from Supelco (Bellefonte, PA, USA) were used (Fig. 1). Due to the strength and dimensions of the Nd magnet used non-special precaution was required.

The statistical software NEMRODW® ("New Efficient Methodology for Research using Optimal Design") from LPRAI (Marseille, France) was used to construct experimental design matrices and evaluate the results.

2.3 Synthesis of magnetic graphene oxide

MGO was synthesized using a newly developed precipitation method. At first, Fe^{2+} and Fe^{3+} ions were adsorbed on dispersed GO nanosheets, and then magnetite nanoparticles were formed and immobilized on the nanosheets surface by increasing pH of the solution with ammonium hydroxide solution (32%, w/w). Typically, $FeCl_3{\cdot}6H_2O$ (0.11 g) and $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$ (0.35 g) were dissolved in 20 mL deionized water (solution A). Also, GO (0.1 g) was dispersed in 200 mL deionized water by sonication for 2 h (solution B). Then, solution A was added to solution B dropwise in 5 min, and the mixture was stirred for 30 min at 90 °C. After that, mixture pH was adjusted to 11 using ammonium hydroxide solution (32%, w/w) to form the magnetite nanoparticles. The mixture was stirred continuously for 4 h, then the magnetic nanomaterial (MGO) was separated using an external magnetic field (neodymium magnet), washed using deionized water and ethanol (3 consecutive times), and dried at 200 °C for 2 h.

Fig. S1 (Supplementary material) shows the magnetization hysteresis loop of GO/Fe_3O_4 and a photograph showing the magnetic attraction between the synthesized composite and the magnet. The magnetization hysteresis loop of GO/Fe_3O_4 was S-like curve indicating that the composite was superparamagnetic material. The specific magnetization saturation (M_s) was 38.5 emu g^{-1}.

2.4 TD-GC-MS conditions

The thermodesorption system was adjusted according to our previously published paper [25] as follows: splitless mode; desorption temperature, from 25 °C (0.5 min) to 240 °C at 60 °C min^{-1}; desorption time, 5 min; helium flow rate, 100 mL min^{-1}; transfer line temperature, 300 °C. The desorbed compounds were cryofocused in the cooled injection system at 0 °C. Then, the temperature was rapidly increased at 12 °C s^{-1} to 250 °C, transferring the compounds to the GC column by operating in solvent vent mode for 1 min. A DB-624 (6% cyanopropylphenyl-94% dimethylpolysiloxane, 30 m, 0.25 mm I.D., 1.4 µm film thickness) analytical column from Agilent Technologies was used with the following oven temperature program: from 70 °C (2 min) at 5 °C min^{-1} to 130 °C, and then at 10 °C min^{-1} to 240 °C (5 min).

The MS detector voltage was set at 1700 V. Electron impact ionization was used with ionization energy of 70 eV. The mass source and quadrupole were set at 230 and 150 °C, respectively. The measurements were carried out in selected ion monitoring (SIM) mode at the following mass/charge ratios: 146 from minute 0 to 14 for dichlorobenzenes determination, 180 and 236 from minute 14 to 18 for trichlorobenzenes and IS, respectively, 216 from minute 18 to

21 for tetrachlorobenzenes and 250 from minute 21 to 23 for PeCB.

2.5 Mag-HSAE-TD-GC-MS procedure

The developed method involves three steps: headspace extraction, thermal desorption and GC-MS detection (Fig. 1). In the case of the headspace extraction unit, 10 mg MGO was homogeneously fixed in one of the 3 mm edge of a Nd magnet (the lower magnet). In order to fix the sorbent, the magnet was gently approached to the MGO, and then, the magnetic material was homogeneously attracted to the magnet according to the magnetic field of the magnet (Fig. 1). The lower magnet was fixed in the headspace of a 25 mL glass vial, containing standard or water samples, 50 ng L^{-1} of IS and a proper stir bar. Another Nd magnet (the upper magnet) was put over the vial cap to fix the lower magnet in the headspace of the samples without any other special equipment. Then, the solution was stirred (at 1500 rpm) for 30 min at room temperature. Next, the lower magnet was manually dropped into the TD glass tube by removing the upper magnet. Then, TD and GC-MS detection were carried out (a typical chromatogram is shown in Fig. 2). The reusability evaluation has been investigated and the results show that the MGO sorbent can be reused; however, carry over effects have been observed. Hence, fresh nanocomposite and new magnets were used for each experiment. Additionally, visual inspection confirmed no sorbent dislodgement during desorption.

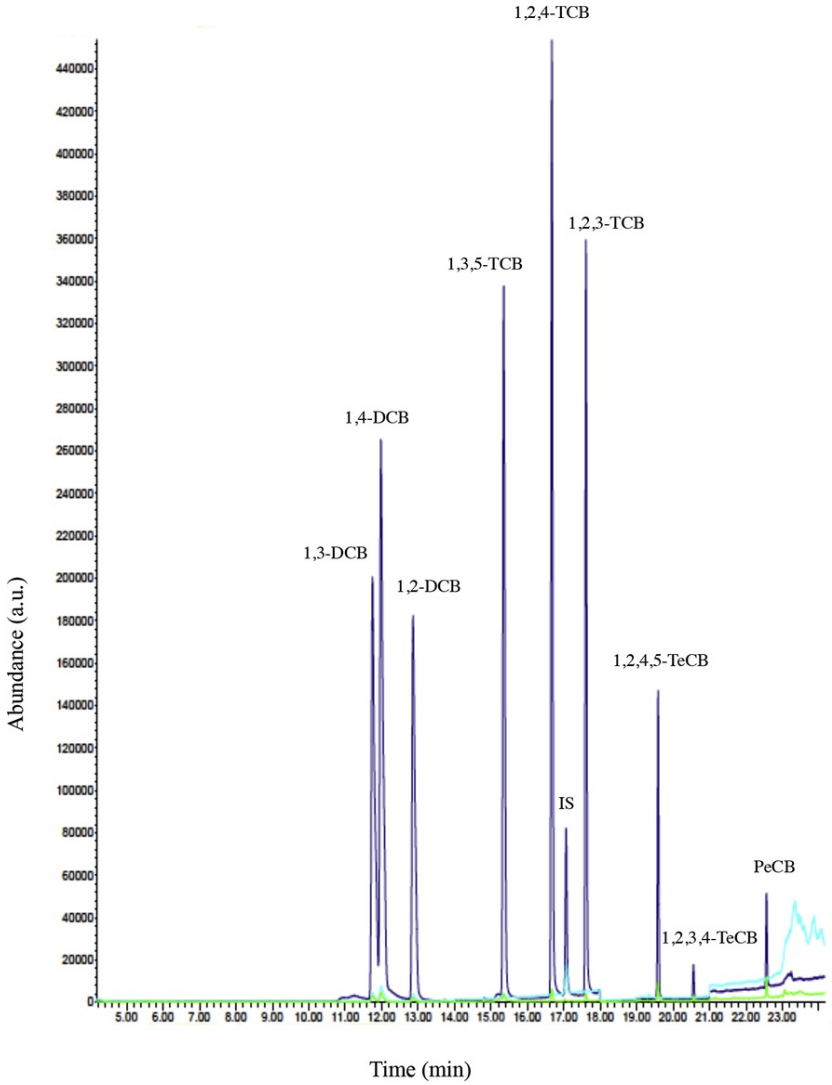

Fig. 2 Total ion chromatograms obtained in the SIM mode after Mag-HSAE of a blank (green line), a wastewater sample (light blue line) and a wastewater sample spiked at 50 ng L^{-1} with target analytes and the IS (dark blue line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

alt-text: Fig. 2

Finally, it is important to point out that extractions using Fe_3O_4 as extractant phase (without GO) were carried out and chlorobenzenes were not detected, showing that Fe_3O_4 did not possess any sorption capacity for target analytes.

3 Results and discussion

3.1 Characterization of the synthesized magnetic nanomaterial

Fig. S2 shows the TEM images of the nanomaterials. The TEM image of bare graphene oxide nanosheets is presented as Fig. S2a while Fig. S2b shows the nanosheets decorated with magnetite nanoparticles. As can be seen, the nanosheets are almost uniformly modified by the magnetic nanoparticles with an average size of 14 ± 3 nm.

The XRD pattern of the synthesized magnetic nanomaterial is presented in Fig. S3. The XRD pattern of the synthesized MGO (Fig. S3b) shows diffraction peaks that are indexed to (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) reflection characteristics of the cubic spinel phase of Fe_3O_4 (JCPDS powder diffraction data file no. 79-0418), revealing that the resultant MGO are successfully loaded by mostly magnetite nanoparticles [26].

3.2 Mag-HSAE optimization

The considered parameters that could potentially affect extraction were: sample volume, extraction time, temperature, ionic strength, MGO amount and stirring speed. Temperature was excluded based on our previous work, which showed the non-significant effect of this factor [27], hence, the experiments were carried out at room temperature (21 °C). The rest of these parameters were studied and optimized by means of an experimental design [28]. The Plackett-Burman design is a two-level fractional factorial design that ignores the interaction between factors and, therefore, main effects can be calculated with a reduced number of experiments, leading to a saving in resources and time [28]. A Plackett-Burman design was used to construct the matrix of experiments, and the five factors selected at two levels were: sample volume, extraction time, MGO amount, ionic strength and stirring speed. Table 1 shows the experimental factors and levels considered in the Plackett-Burman design. In total, eight experiments were randomly performed using aqueous standards of 1 μg L^{-1} and the peak area of each chlorobenzene was used as response function.

Table 1 Experimental factors and levels of the Plackett-Burman design.

alt-text: Table 1

Factor	Level	
	Low	High
Sample volume (mL)	5	20
Extraction time (min)	5	30
MGO amount (mg)	1	10
Ionic strength (NaCl concentration; %, w/v)	0	15
Stirring speed (rpm)	500	1500

The data obtained were evaluated by ANOVA test and the results were visualized by using the Pareto charts of main effects shown in Fig. 3. Fig. 3 shows the charts for 1,2-DCB, 1,2,4-TCB, 1,2,4,5-TeCB and PeCB. Charts of 1,3-DCB and 1,4-DCB, 1,3,5-TCB and 1,2,3-TCB, and 1,2,3,4-TeCB are shown in Supplementary material (Fig. S4) since they were similar to 1,2-DCB, 1,2,4-TCB and 1,2,3,4-TeCB, respectively. In Fig. 3 and Fig. S4 the bar lengths are proportional to the absolute value of the estimated main effect, and the positive or negative sign reveals the cases where the instrument's response can be enhanced or reduced, respectively, on passing from the lowest to the highest level set for the specific factor. Furthermore, an effect which exceeds the vertical reference line, corresponding to the 95% confidence interval, may be considered significant with regard to the response. In some cases, the vertical reference line does not appear if the effect of the variable is far from the significance level. None of the factors exceed the vertical line for any Pareto chart, which means that the parameters studied show a non-significant effect upon

extraction.

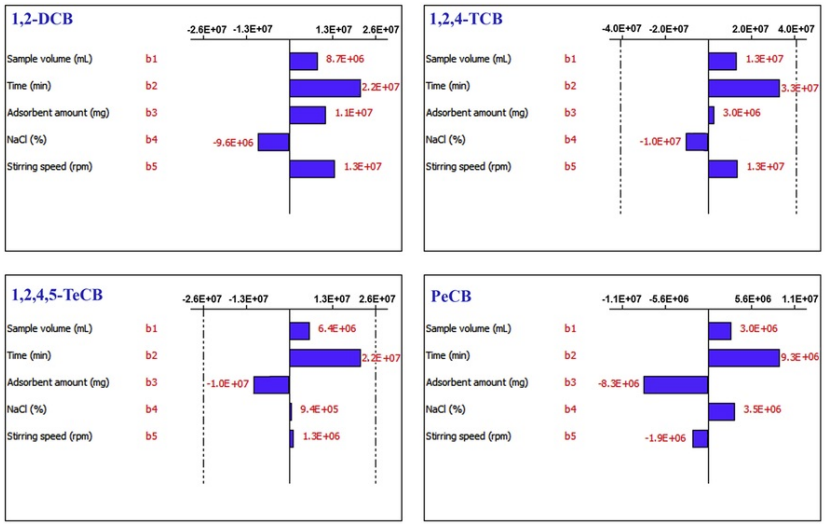

Fig. 3 Pareto charts of the main effects obtained from a Plackett-Burman design for 1,2-DCB, 1,2,4-TCB, ~~1,2,3,4-TeCB~~1,2,4,5-TeCB and PeCB.

alt-text: Fig. 3

As shown in Fig. 3 and Fig. S4, sample volume and extraction time showed a positive effect for the nine chlorobenzenes. Accordingly, increasing the aqueous sample volume and extraction time resulted in an increase in the total amount of target pollutants transferred in the headspace, thus enhancing preconcentration [27,29]. Therefore, these factors were established at a high level, 20 mL, and 30 min, respectively. MGO amount showed a positive effect for di- and tri- but a negative effect for tetra- and pentachlorobenzene. Stirring speed showed a positive effect for di-, tri- and 1,2,4,5,-TeCB but a negative effect for 1,2,3,4-TeCB and pentachlorobenzene. Apart from affecting positively to most of the analytes, a common experimental set of conditions should be used for the analytes. Fig. S4 shows the Pareto chart obtained for the sum of areas as the response function. In this case, ~~ab~~sorbent amount and stirring speed showed a positive effect. Higher amounts of sorbent increased adsorption capacity and increased speed of sample stirring was expected to enhance the rate of extraction of all target analytes. By contrast, ionic strength showed a negative effect for di- and tri- and positive for tetra- and pentachlorobenzene, and also negative for the simultaneous optimization of all analytes (i.e., goal function as sum of areas). For this reason, NaCl addition was not considered. As a conclusion, the optimum conditions of the Mag-HSAE procedure, considering the individual areas or sum of areas as a goal function (Fig. S4), were: sample volume, 20 mL; extraction time, 30 min; MGO amount, 10 mg; NaCl concentration, 0%, and; stirring speed, 1500 rpm.

3.3 Analytical parameters

A linear calibration was obtained for each chlorobenzene by plotting the ratio of the peak area of the analyte to peak area of the internal standard versus concentration of the analyte under the optimum experimental condition (Fig. S5). The calibration parameters, extracted from the calibration curves with determination coefficients (R^2) higher than 0.99, are shown in Table 2.

Table 2 Analytical parameters of the investigated chlorobenzenes using the proposed Mag-HSAE-TD-GC-MS method.

alt-text: Table 2

Analyte	Dynamic range (ng L^{-1})[a]	Slope (area units L ng^{-1})	Determination coefficient (R^2)	CV (%)[b]		LOD (pg L^{-1})	LOQ (pg L^{-1})
				10 ng L^{-1}	50 ng L^{-1}		
1,3-DCB	0.5–100 (6)	0.1038	0.994	3.9	2.8	125	417
1,4-DCB	0.5–100 (6)	0.1266	0.992	3.3	3.2	93	310

1,2-DCB	0.5–100 (6)	0.0856	0.993	4.2	3.4	173	577
1,3,5-TCB	0.5–100 (6)	0.1048	0.994	4.5	1.5	193	643
1,2,4-TCB	0.5–100 (6)	0.0804	0.991	9.5	6.3	131	437
1,2,3-TCB	0.5–100 (6)	0.0547	0.992	8.9	4.2	153	510
1,2,4,5-TeCB	0.5–75 (5)	0.0159	0.996	7.7	3.6	134	447
1,2,3,4-TeCB	1-75 (5)	0.0018	0.993	8.7	7.5	301	1003
PeCB	0.5–75 (5)	0.0071	0.992	7.0	5.4	149	497

[a] Number of calibration points in parentheses.

[b] n = 5.

The limit of detection (LOD) and limit of quantification (LOQ) are defined as LOD = $3S_b/m$ and LOQ = $10S_b/m$, where S_b and m are the standard deviations of the blank and the slope of the calibration graph, respectively. LOD values ranged between 93 and 301 pg L^{-1} and LOQ values ranged between 310 pg L^{-1} and 1 ng L^{-1}. The repeatability of the measurements was evaluated by extracting five consecutive standard aqueous solutions at 10 and 50 ng L^{-1} concentration levels. The obtained coefficients of variation (CV) (Table 2) varied between 1.5% ~~1.5%~~ and 9.5% ~~9.5%~~, showing acceptable repeatability, bearing in mind that the concentrations were at ultra trace levels.

As can be seen from Table 2, the method provides the lowest sensitivity (based on the calibration curve slopes) for high molecular weight compounds (i.e., 1,2,4,5-TeCB, 1,2,3,4-TeCB and PeCB). Based on Henry's law constants [30], volatilities of the investigated compounds follow this order: PeCB≫1,2,4-TCB>1,3-DCB>1,2,4,5-TeCB≈1,2,3,4-TeCB>1,2,3-TCB>1,2-DCB>1,4-DCB≈1,3,5-TCB. But, in contrast, on increasing the number of chlorine substitutes, the benzene ring charge density decreased. Nevertheless, high molecular weight compounds have a stronger tendency to escape from solution phase, but their π-π interaction with the graphene oxide nanosheets is still weaker than the lower molecular weight chlorobenzenes. Therefore, high molecular weight chlorobenzenes have lower extraction efficiencies. However, the proposed method still provides very low detection limits for the investigated compounds compared to previously reported works (Table 3).

Table 3 Comparison of the developed Mag-HSAE-TD-GC-MS method with some previously reported headspace extraction methods for analysis of chlorobenzenes in aqueous samples.

alt-text: Table 3

Extraction method	Dynamic range (ng L^{-1})	LOD (ng L^{-1})									CV (%)	Extraction Temp. (°C)	Extraction time (min)	Detection method	Ref.
		1,3-DCB	1,4-DCB	1,2-DCB	1,3,5-TCB	1,2,4-TCB	1,2,3-TCB	1,2,4,5-TeCB	1,2,3,4-TeCB	PeCB					
G-SPME	2500–500000 2500–800000	800	–	500	–	500	–	–	–	–		20	15	GC-FID	[31]
IL-SDME	5000–160000	152	203	102	122	122	102	102	102	–	1.6–5.1	RT	37	LC-UV	[27]
Dodecane-HSME	500–3000 5000–30000	100	3000	200	–	–	–	–	–	–	<10	45	5	GC-ECD	[32]
PS-SPME	240–24000 5–500 0.5–20	–	75	40	–	1.5	–	–	0.15	–	2.1–9.7	35	5	GC-ECD	[33]
MW-SDME	1000–320000	32	39	24	22	22	16	16	16	–	2.3–8.3	21	20	LC-UV	[29]
PC-SPME	250–250000 490–250000	31	–	62	–	62	–	–	–	–		40	30	GC-FID	[34]
PU-SPME	50–900 50–1000	–	10	10	–	10	10	–	10	–	3–11.3	30	10	GC-MS	[35]

PDMS-SPME	20–20000	6	6	6	4	4	4	3	3	4	1.2–8.2	RT	30	GC-MS	[3]
HSSE	7–1000	6	4	2	4	7	9	7	11	12	5–10	RT	60	GC-MS	[36]
Toluene-SDME	20–50000	3	6	6	4	6	6	3	3	16	2.1–13.2	RT	5	GC-MS	[37]
IL-SDME	20–2500 20–5000 20–10000 20–15000	3	2	2	4	2	2	2	2	1	2–17	RT	37	GC-MS	[25]
CA-SPME	8–800 80–8000	–	–	–	2.25	1.64	0.94	1.26	0.32	0.50	2.1–4.9	20	15	GC-ECD	[38]
PPy-SPME	5–1000 2.5–1000	–	0.8	0.8	–	0.6	–	–	0.5	–	3–14	65	25	GC-MS	[39]
MOF/PANI-SPME	0.5–1000	–	0.2	0.1	–	0.1	0.1	–	0.1	–	5–8	25	20	GC-MS	[40]
Mag-HSAE	0.5–100 0.5–75	0.12	0.09	0.17	0.19	0.13	0.15	0.13	0.30	0.15	1.5–9.5	RT	30	GC-MS	This work

G-SPME, graphene composite coated stainless-steel wire, IL-SDME, ionic liquid-based single-drop headspace microextraction, Dodecane-HSME, dodecane based headspace solvent microextraction; PS-SPME, polysiloxane coated steel fibers; MW-SDME, microwave-assisted headspace SDME; PC-SPME, polycarbazole coating platinum wire; PU-SPME, polyurethane nanofibers coated SPME fiber; PDMS-SPME, poly(dimethylsiloxane) coated SPME fiber; HSSE, headspace sorptive extraction using silicone tubes; CA-SPME, diglycidyloxycalix [4]arene coated SPME fiber; PPy-SPME, polypyrrole film containing dodecyl sulfonate coated stainless steel wire; MOF/PANI-SPME, metal organic framework-polyaniline nanocomposite coated stainless steel wire; LC-PDA, liquid chromatography with photodiode array detector; LC-UV, liquid chromatography with UV detector; GC-ECD, gas chromatography with electron capture detector; GC-MS, gas chromatography-mass spectrometry; GC-FID, gas chromatography with flame ionization detector; RT, room temperature.

As can be seen from Table 3, the present method provides the lowest detection limits among the compared methods. However, this is not the only advantage of this method over the previously reported ones. For example, Mag-HSAE technique does not require tedious steps to ~~precondition~~ preconcentrate the analytes or to fix the extraction unit ~~or~~and to adjust the extraction material in sample headspace, it avoids solvent evaporation problems or the need to protect the extraction material. Other advantages of Mag-HSAE are simplicity in setup and operation, its cost effectiveness in extraction and its in-situ sampling ability. It is notable that in Mag-HSAE only 10 mg of the adsorbent is needed for each experiment, and due to the MGO, relatively cheap precursors and simple synthesis procedure it is very cost effective.

3.4 Real water samples

In order to assess the applicability of Mag-HSAE-TD-GC-MS for the determination of chlorobenzenes in real samples, three real water samples (i.e., tap, mineral and effluent water samples) were analyzed. Preliminary analysis revealed that chlorobenzenes were not present at detectable concentrations in the investigated samples (Fig. 2). Thus, they were spiked with the target chlorobenzenes and IS at 50 ng L^{-1} level and were analyzed under the optimum experimental condition (Fig. 2). Relative recoveries were determined as the ratio of the concentration found in real and deionized water samples both after extraction. The values were in the 86–110% range (Table 4), indicating non-significant matrix effects on the extraction performance of the Mag-HSAE method for extraction of the investigated chlorobenzenes.

Table 4 Real water samples analysis by the Mag-HSAE-TD-GC-MS method.

alt-text: Table 4

Analyte	Relative recoveries[a] (%) and CV in parenthesis (%)		
	Tap water	Mineral water	Effluent water
1,3-DCB	103 (2.1)	108 (2.8)	98 (3.6)
1,4-DCB	97 (4.3)	105 (3.2)	101 (4.5)

1,2-DCB	110 (2.6)	104 (3.4)	95 (3.7)
1,3,5-TCB	95 (4.5)	101 (1.5)	103 (2.6)
1,2,4-TCB	109 (3.4)	94 (6.3)	86 (5.3)
1,2,3-TCB	105 (2.8)	108 (4.2)	96 (7.2)
1,2,4,5-TeCB	97 (5.3)	98 (3.6)	87 (6.5)
1,2,3,4-TeCB	95 (5.2)	102 (7.5)	90 (4.3)
PeCB	103 (8.1)	100 (5.4)	105 (4.4)

[a] Mean value of three extractions at 50 ng L^{-1} concentration level.

4 Conclusions

A new Mag-HSAE technique using graphene oxide/iron oxide composite as sorbent deposited on one end of a neodymiun magnet has been proposed in this work. The composite-neodymium magnet set-up presents remarkable advantages such as low cost, rapid and easy handling and portability. Additionally, sorbent synthesis is a simple procedure. To our knowledge, this is the first time that Mag-HSAE has been employed as an extraction technique with chlorobenzenes selected as model compounds having been preconcentrated from water samples. Good extraction efficiencies were obtained which provide excellent LOD values, lower than those previously reported for the same analytes and detection method. Finally, our study demonstrates the proposed method is able to determine chlorobenzenes at trace levels in real water samples. This new sample preparation technique possesses unique and promising properties for headspace solid-phase extraction of target analytes prior to the use of separation-detection instruments, such as GC and LC. Additionally, different magnetic sorbents in liquid or solid state can be used in different situations for simple, fast, sensitive and cost effective headspace extraction of a wide range of analytes from different matrixes.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.aca.2017.04.002.

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Appendix A. Supplementary data

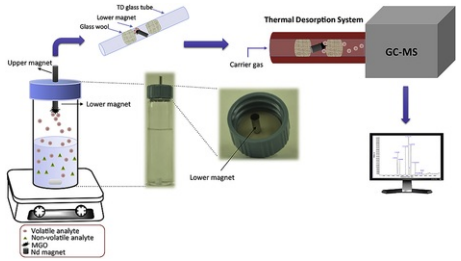
The following is the supplementary data related to this article:

Multimedia Component 1

Supplementary material

alt-text: Supplementary material

Graphical abstract



alt-text: Image 1

Highlights

- A new extraction technique named Magnetic Headspace Adsorptive Extraction is presented.
- Graphene oxide/iron oxide composite deposited on a neodymiun magnet as sorbent.
- Sorbent of low cost, rapid and simple synthesis, easy manipulation and portability options.
- Fast and efficient extraction and sensitive determination of chlorobenzenes in water samples.

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